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(54) Title: MODIFICATION OF METALLIC PARTICLES

(57) Abstract

Powders of milleable metal, particularly zinc, are milled with a dry solid lubricant to form flakes. The final product is obtained much more cheaply than with conventional flaking processes, has a low apparent density and, when the metal is zinc and is incorporated into a corrosion resistant coating, provides a superior product to one produced with conventional zinc powders. In particular, there is a reduced ratio of zinc pigment to binder. The solid lubricants are inorganic lubricants particularly carbon such as graphite or organic lubricants such as film-forming polymers for example polyfluoroethylenes but not materials with surface active groups, e.g. soaps. Where the metal is zinc and the lubricant is graphite or carbon black, the lubricant may be incorporated into the lattice structure of the metal to provide a new form of zinc flake.

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MODIFICATION OF METALLIC PARTICLES

This invention relates to the production of particulate metals. It particularly relates to modification of zinc for use in anti-corrosion compositions.

The outstanding corrosion resistance afforded by application of zinc compositions to steel has made it the most effective means for the long term protection of steel from oxidation (rusting) and subsequent corrosion. It is a conventional method of providing protection for products such as guardrails and transmission towers and dozens of other applications.

The usage of zinc for cathodic protection against oxidation and corrosion creates a worldwide annual consumption of zinc of 3.6 billion kg (8 billion lbs) of zinc annually.

Zinc can be applied by a so-called galvanizing process in which the zinc is applied by, for example, hot dipping or electroplating. Galvanizing employing pure zinc without a binder has provided the best protection with maximum corrosion resistance. However, it is desirable where possible to apply the zinc by means of a surface coating. Galvanizing coating compositions, also referred to as "zinc-rich primers", contain zinc metal particles and become oxidized only when exposed to the elements. Conductivity of the galvanizing composition provides an excellent cathodic protection to steel (and which acts as the cathode, zinc being the anode) when exposed to a saline environment or other forms of oxidation caused primarily by water in its various forms, for example moisture, vapour or ice.

Zinc-rich primers have been considered to be optimum anti-corrosion coatings on iron or steel substrates but such compositions do have problems. To insulate the zinc particles from each other and from the substrate, it is considered necessary to use in the compositions zinc to binder ratios by weight of at least 8.5:1.5 to 9.5:0.5. With this high zinc level

and with the relatively high density of zinc there can be undesirable settling during storage. Zinc is often added to compositions just prior to use and mixed rapidly during application to prevent settling and clogging of equipment.

Another limitation of primers has been that they have traditionally been limited to application over blasted and untreated steel. However, steel is often "passivated". Passivation promotes adhesion to metal and includes the application of zinc phosphate or iron phosphate to the steel substrate. Zinc rich primers are not usually applied over iron phosphated steel since these primers do not possess sufficient conductivity to provide cathodic protection to iron phosphated steel.

Zinc metal is used in coating compositions in particulate form. Conventional forms of particulate zinc, although effective in zinc coating compositions to provide cathodic protection, tend, as stated, do require high proportions of zinc to binder.

These problems associated with the manufacture of storage and handling cost and application of these primers have limited their utilisation to about 26.5 million litres (7 million US gallons) annually worldwide. In particular these problems have limited use of primer technology to use of coating compositions requiring a blasted substrate.

It would be desirable to improve primer technology including cost, density and ease of manufacture while improving overall cathodic quality thus promoting superior anti-corrosion properties.

Other metals which are used in particle form also have problems arising from the current particle shapings available in commerce, particularly high apparent density.

The object of the present invention is to provide improved

metal particles and a more efficient method for the production of such metal particles.

A particular object of the invention is to provide a new form of zinc particle and a method of producing such particles. This aspect of the invention also provides improved coating compositions containing such particles.

Compositions have been disclosed in which, in addition to the content of zinc, other components are added to modify the electrical conductive characteristics. For example, in US Patent No. US-A-4,891,394 issued January 1990 to the applicant of the present invention there is disclosed a coating composition containing 30 to 60% by weight metallic zinc and an agent for control of electrical conductivity characteristics comprising a crystalline silica. Other patents include US Patent No. US-A-3,998,771, issued December 1976 to T.J. Feneis Ar. et al., US Patent No. US-A-4,417,007, issued November 1983 to G. Slaensky et. al., US Patent No. US-A-4,885,324 issued December 5th, 1989 to Hegedus et. al., US Patent No. US-A-4,748,194 issued May 1989 to Geeck, US Patent No. US-A-4,621,024 issued November 4th, 1986 to F.A. Wright, US Patent No. US-A-5,182,318 by the applicant of the present application, Canadian patent CA-A-2,065,828 and US Patent No. US-A-5,167,701 issued December 1992 to applicant of the present invention.

US Patent No. US-A-4,474,685 issued October 2nd, 1984 to N. Annis discloses a multi-component electro-conductive filler containing at least two members from the group of particles of carbon black and graphite and conductive metals such as zinc. Canadian patent CA-A-2,074,329 mentions the use of lamellar zinc (zinc flakes).

The use of graphite as part of the system is known to result in improved overall electrical conductivity, lower overall

specific gravity of the coating, improved tensile strength, flexibility, corrosion resistance and water vapour impermeability.

In US Patent No. US-A-5,677,367 granted to the present inventor on October 14th, 1997 there is disclosed a composition containing zinc dust or zinc powder and graphite powder in which the zinc percentage as part of the combined amount of zinc and binder is from 75 to 90% and graphite is present at about 20 to 60% of binder by weight. The compositions including binder are prepared by simple mixing, for example in a two screw extruder. The resulting compositions can be used for electrostatic spraying of powdered compositions. Zinc powder and zinc dust used in the disclosure of this patent is distinguished from lamellar zinc or zinc flakes as used in the Canadian patent CA-A-2,074,329 mentioned above.

Introduction of graphite while improving results requires a high percentage of carbon to binder (possibly 40 to 50% by weight). The use of graphite while giving improved results only reduces the ratio of zinc to binder from 9:1 by weight zinc to binder to 8:1. The high content of graphite may cause the zinc to be exhausted more readily and may make top-coating mandatory.

The following patents disclose the presence of graphite for these purposes but only in the context of simple admixtures: US Patent No. US-A-3,838,495 issued October 1st 1974 to Kuhnert, US Patent No. US-A-4,081,423 issued March 28th, 1978 to Hardenfelt, US Patent No. US-A-4,545,926 issued October 8th, 1985 to Fouts, Jr. et. al., US Patent No. US-A-5,284,888 issued 26 February 1994 to Morgan, Japanese Patent Publication No. 24566/74. An improvement on the disclosure of this Japanese patent is Japanese Patent Kokai (laid open) No. 51958/84 where a finely divided carbon is added to improve the physical properties of the film. US Patent No. 5,275,707 issued January 1994 to Yamada et al., which discusses the said Japanese Publications suggests that the presence of graphite in coatings

is undesirable because it reduces rust resistance, increases dispersibility and does not give a uniform, electrically conductive coating film.

In US 5,213,846 issued May 1993 to Tsuneta et al., there is disclosed a composition containing graphite particles to enhance welding. Again this patent suggests that graphite may lead to detrimental effects on corrosion resistance for the composition.

US Patent No. 4,411,742 issued October, 1983 to Donakowski et al., discloses a lubricant composition containing zinc and graphite although it has a higher resistance to corrosion. The composition is applied as a co-deposit by electroplating zinc in the presence of an electrolyte containing zinc ions and bulk graphite. The graphite saturates the zinc interface as it plates out. US Patent No. 4,411,742 also discloses forming electro co-deposited zinc/graphite coatings, the graphite being present in the amount of 30 to 48% by weight of the co-deposit which is stated as being critical. However, the addition of graphite in such a composition reduces corrosion resistance. The composition is an electrolytic co-deposit as distinct from a composition for use in providing primers or other coating compositions.

Organic coatings made using particulate zinc provide only limited protection to bare metal due to their much lower conductivity than zinc metal which is caused by the dielectric properties of organic resins. In conventional zinc rich paints or primers, the greater the conductivity the greater the area of adjacent bare steel that will be protected by the zinc metal. The level of adjacent bare metal protection is largely proportional to its conductivity measured in Ohms/cm^2. All galvanizing compositions prior to exposure will measure total conductivity of 0.00 Ohms/cm^2 at 75 micron deposition whereas zinc particulate-rich industrial and maintenance coatings will measure from 1 to several dozen Ohms/cm^2 of 75 microns based on the percentage of zinc particulate material and the particle size of the zinc utilised. Hitherto in order to provide adequate

cathodic continuity, zinc has been incorporated into binders in amounts of from 80 to 95 weight percent of zinc by total weight of zinc plus binder not including other additives. However, the high percentage of zinc, although providing improved conductivity, creates serious problems from the high density and low binder content both in handling and adhesion to the substrate. In single component inorganic compositions, the nature of the binder is such that it is triggered by exposure to moisture which can take place at the time of addition of zinc. These compositions are often manufactured in inert environments which again causes increased cost.

Conventional zinc is provided in the form of dust or powder. The former is usually prepared by condensation of zinc vapour in an inert atmosphere. Depending on the purity of the starting zinc material, the nature of the condensing system and purging of the system may have to be modified to provide for the necessary quality of zinc. The particle size is usually less than 20 microns.

Zinc powder is usually produced by breaking up a stream of molten zinc metal into droplets by impact of a pressurised stream of fluid, usually air, on the zinc stream. This process requires large volumes of fluid and collection techniques to collect any particles which do not settle out of the gas stream. Usually the particle size is from 20 microns to 60 microns.

Zinc rich primers particularly those which are organic film forming compositions manufactured with zinc dust (or zinc powder) tend to provide only thin adjacent protection to exposed bare metal (limited to a scribed area). This is believed to be because of zinc dust's lower conductivity caused by surface oxidation.

A convenient method of testing is to drill several holes of 6-8mm through the primer coating to bare metal and expose the resulting primed panel to the ASTM B-117 salt-fog test. In the

ASTM test a primed scribed panel coated with primer over 100 bonderised or blasted steel is subjected to 5% sodium chloride salt-fog for a predetermined period. However, the conventional ASTM method of testing may be misleading since the scribed area of bare metal exposed to salt fog is extremely thin and one may obtain impressive results because the primer produces deposits of zinc oxide, zinc carbonate (white rust) in the scribed area. The modified test method allows anti-corrosion properties to be determined on less than 500 hours as compared to the thousands of hours previously necessary.

A lamellar form of zinc, namely zinc flake, can be formed by ball-milling in a non-reactive fluid such as a hydrocarbon normally in the presence of a lubricant, for instance stearic acid. The milling flattens the zinc particles. The usual starting material is zinc dust and the milling produces a flake of thickness of 1 micron or smaller and an aspect ratio ie. diameter to thickness of about 10. This type of wet milling is described in French Patent FR-A-1570616 British Petroleum (Chemical Abstract 72-45774)

The process, however, has a number of disadvantages. It is not very rapid. The materials of construction for the ball-milling must be chosen to avoid contamination. The operation involves the use of a flammable fluid, for example a hydrocarbon such as mineral spirits, which creates environmental problems when it is removed. Thus the hydrocarbon can amount to 40% volume must be evaporated. As a result, the capital cost of a flaking plant is very high per unit of production. This and the small volume of flake manufactured by such a plant makes the cost of the material high which tends to limit its application. Moreover the stearate in the product interferes with the compatibility of the zinc with the other components of the coating composition. This is believed to arise from the fatty component of the stearate.

The use of zinc flake for coating compositions is disclosed

in US Patent US-A-4,799,959 (Fourez et al) but merely as a raw material for coatings for threaded devices. Combinations of flakes (manufactured by wet milling) in amounts of less than 50% by weight with zinc dust are disclosed in US Patent 4,891,268 (Durand).

On the other hand, it has been found that the quality of cathodic protection provided by zinc flake as compared to zinc dust or zinc powder permits a considerable reduction of the weight of pigment binder to produce comparable cathodic protection. Thus zinc flake can reduce the density of zinc in the coating composition by as much as two thirds although the volume of zinc, because of the milling process, remains approximately the same. Nevertheless, because of the complexity of the cost of the processes of producing zinc flake as outlined above, the resulting zinc flake has been too expensive to replace zinc dust and zinc powder in conventional zinc rich primers except as a limited proportion of the zinc pigment. The cost per pound of zinc flake tends to be six to seven times the price of zinc dust. Consequently, despite the dramatic reduction in density that can be accomplished by utilising a large percentage of total flake in the formula, the resultant material cost is not competitive with conventional organic or inorganic zinc rich primers. Consequently the use of zinc flake has been limited to certain specific applications.

For other metals used in fine particle form the tendency has been to examine the desirable properties from the point of view of appearance. The method of wet flaking outlined above gave a product which had visual attractiveness. When a product of low apparent density was desired it was therefore reasonable to employ such traditionally produced products.

However, a low apparent density product not contaminated with organic grinding agents and not requiring removal of large quantities of organic solvent materials has been found to be very valuable.

By apparent density is meant that the particles in bulk loose form have a weight for volume which may differ from the density of masses of the material. The spacing created between particles by reason of shape of particles alters the apparent density.

It has now been found that, if there is used in the milling of metal particles to form particles in flake form, a dry solid lubricant, for example graphite or carbon black or polyfluoroethylene, the resulting flake is produced more economically, has a lower bulk density and is usually more effective than mètal flakes produced by wet grinding processes.

This particularly applies to zinc especially when ground with graphite or carbon black as the grinding agent due to their conductive properties.

In particular, it has now been found that for many, if not all inorganic lubricants the resulting zinc flake proves to be more effective than unmodified zinc flake. It would appear that the inorganic lubricant, particularly carbon, especially graphite, is incorporated into the metal of the zinc particles at least to some degree whereby the resulting composition is a very effective zinc component in anti-corrosion compositions. This incorporation into the metallic structure appears also to be found with the other metals.

Other solid lubricants may not be incorporated into the metallic structure but are still useful.

According to the present invention there is provided a method for the preparation of a metal material comprising a metal which is sufficiently malleable for its particles to flatten when subjected to mechanical milling, characterised in that it

comprises a step in which a mixture of particles of the metal and a solid composition with lubricant properties is subjected to mechanical milling under substantially dry conditions until the metal is in the form of flakes.

Further according to the present invention there is provided a finely divided metal flake material characterised in that it comprises particles of a metal which is sufficiently malleable for particles thereof to flatten when subjected to mechanical milling and a solid inorganic lubricant, a major proportion of the lubricant being incorporated into the lattice structure of the metal.

In a specific and particularly important form of the invention the metal is zinc.

In a particular form of the invention, there is provided a composition comprising zinc flakes and graphite or carbon black in which at least a proportion of the graphite is incorporated into the metallic structure of the zinc particles.

The invention also relates to an anti-corrosion coating composition containing the zinc/inorganic lubricant particulate material of the invention. The balance of the composition comprises conventional components, eg. binders, curing agents and dispersants and similar products.

Specifically therefore there is provided a method of preparing an anti-corrosion coating composition comprising the steps of (1) mixing zinc particles with particles of solid components with solid lubricant properties; (2) subjecting the mixture to mechanical milling under substantially dry conditions to render the particles into lamellar shape; and (3) combining said lamellar shaped particles into binder components to form a coating composition applicable to a substrate to form a corrosion resistant surface layer.

In one embodiment of the method of the invention the metal particles and a dry inorganic lubricant are combined and mechanically milled together to produce metal flakes in such a way as to incorporate a major part of the lubricant intimately with the final metal particles.

In one preferred form, zinc particulate material composition containing graphite is milled to incorporate a major proportion of the graphite or carbon black into the zinc flake particles.

The inclusion of the lubricant material, for example carbon, into intimate combination in the zinc particle is an important feature of this aspect of the invention since simply combining zinc powder and free carbon, eg. graphite, while giving useful results requires high proportions of carbon, for example 30% by weight on binder and/or high proportions of zinc flake.

In another important embodiment the lubricant is a fluorocarbon polymer, eg. a polyfluoroethylene.

Another embodiment is a lubricant which is a mixture of fluorocarbon polymer (eg. polyfluoroethylene), carbon (eg. graphite) and, possibly, a silica such as mica.

The introduction of the lubricant, especially graphite, apart from producing a superior final composition, has a dramatic effect on the time and steps necessary for the milling of the metal to a flake form. The ability to operate a mill, for example a pebble or ball mill, for only a few hours (down to about 5 hours with a large commercial mill) is considerably less time than present milling techniques and therefore significantly reduces the cost of flake. The method of the invention is suitably performed using "dry milling", ie. milling in the substantial absence of liquid media. A suitable milling operation is described in detail in Example 14.

Solid lubricants are a well recognised group of lubricants. They are distinguished from liquid or semi-liquid lubricants such as oils and greases (for example hydrocarbons or silicones).

In the case of inorganic lubricants there are generally recognised to be three classes of solid lubricant materials:
1. Layer-lattice solids: the most common are carbon materials such as graphite or carbon black but other lattice structural materials such as molybdenum disulfide, tungsten disulfide, mica, boron nitride, borax, silver sulfate, cadmium iodide and lead iodide have the necessary structure. Whether all of these are usable in all versions of this invention will perhaps require testing to ensure there is no interference with properties relevant to the intended use of the final metal flake but such testing is simple.
2. Soft solids: these include white lead, lime, talc, bentonite, silver oxide and lead monoxide. As in the first group, there may be some of these which, although lubricants, would not be suitable because of intended use of the flake.

Within this group are soft metals such as lead, tin or indium. It is doubtful if all of these can be employed because of their effects on the use of the flake.
3. Chemical conversion coatings: it has been suggested that coatings formed on a metallic surface, for example a sulphide or chloride could provide "lubricated surfaces". This concept does not appear to fall within the term "solid lubricant" as used in this application since they are formed on the surface of a metal article and not added to metallic particles to be milled to alter the shape of the particle.

Organic materials which can be employed as solid lubricants are usually divided into two classes -

(1) Preferred for this invention are polymeric, ie. high molecular weight, film materials particularly polyhaloalkylenes

especially polyfluoroethylenes such as polytetrafluoroethylene or polychlorofluoroethylene. These high molecular weight synthetic polymers, especially polytetrafluoroethylene have been found to provide excellent lubrication for the milling. With zinc they have been found to produce desirable visual properties.

Thus it has been possible to reproduce with polyfluoroethylene as solid lubricant the bright leafing properties of wet milled zinc flake (an appearance similar to aluminum). Milling with polyfluoroethylene as lubricant produces a product which has slightly poorer conductivity products as compared to one using carbon (graphite) as lubricant but a better appearance.

An important feature of zinc milled using polyfluoroethylene as lubricant is that a corrosion-resistance coating made with this material improves welding properties. This is important in automotive primers. For example up to 2000 welds can be obtained. Graphite lubricated zinc flake apparently affects the welding tips adversely.

However, fluorocarbon polymers are relatively expensive. The expense of using them as lubricants can be reduced by using as a lubricant a mixture with one or more inorganic lubricants, for example a mixture of polytetrafluoroethylene, graphite and mica has been very effective for many applications.

A preferred mixture is a 1:1:1 composition.

(2) Soaps, waxes and fats - These materials have been suggested as solid lubricants but are generally inappropriate for this invention because of interference with the properties of the flaked metal. The nature of the interference is not always clear. The problem is possibly due to the presence of oil-compatible groups which, although important for certain surface active functions, can interfere with functionality of a flaked product of the invention in terms of combinability with binders

in coating compositions. The term "interference functionality" signifies that the solid lubricant is free of such groups as would significantly increase the resistivity of the zinc flake product requiring a larger amount of zinc flake in the coating composition and also diminishes the combinability of a zinc flake with coating composition components as compared to dry milling with graphite or a high molecular weight polymeric dry grinding lubricant such as polytetrafluoroethylene. Another problem concerning the utilization of a grease such as stearic acid is that it is reactive with waterborne silicates (potassium, sodium, lithium etc.,) seriously reducing the potlife when the zinc flake is added. Graphite and flouro carbons have no negative effect on binders with a high pH such as the silicates and other waterborne binders.

It is a matter of simple comparative testing to check whether a particular known or possible organic solid lubricant is usable in the method of the invention.

Those solid lubricants of this class which contain interference functionality are therefore excluded. Simple solid hydrocarbons as waxes are probably also not usable as they are not resistant to the heat generated in the milling process. High molecular weight (polymeric) silicones may be suitable.

A small amount of a dispersing agent, for example a stearate, may be added to the lubricant (see Example 4) merely to assist in dispersing lubricant in the solid mixture of components. This is substantially less than amounts used in wet milling and, in itself, would not be sufficient to act as a lubricant. The requirement of absence of interference functionality can therefore apply to either the whole of the material of solid lubricant or the overall characteristics of a combination of materials.

A solid lubricant as used in this invention must therefore be (particularly for organic lubricants) one which is appropriate

for dry milling of a metallic material to a flake which is to be used in coating compositions. This implies heat resistance and absence (in organic materials) of interference functionality.

An inorganic lubricant can sometimes be referred to as a lubricant with electrical enhancing properties. It is known to incorporate certain inorganic materials which have an effect on the cathodic protection which zinc provides in anti-corrosion compositions. Such materials include forms of carbon, forms of silica, particularly hydrophobic silicas and metallic oxides, for example aluminum oxide. For use in this invention such cathodic activity enhancing inorganic materials must have some lubricant properties which allows milling of the zinc particles to flake form while avoiding fusion of the zinc. Any inorganic material which provides the appropriate lubricant action for dry milling zinc can be employed and it does not appear necessary to employ a compound which has a negative effect on the cathodic properties of zinc. Determination of appropriate materials is not difficult given the teaching of this application and the knowledge of those skilled in the art as to dry lubrication.

For metals other than zinc the choice of inorganic lubricant is likely to depend only on the lubricant properties.

Certain inorganic lubricants, for example carbon, can be introduced into the zinc flake particles by forming a zinc/carbon composition from which particulate flake zinc is formed under conditions in which at least some of the carbon present is intimately incorporated into the metallic structure of the final zinc particles. The carbon could be in the form of graphite or conductive carbon black. Although carbon is the preferred inorganic lubricant, other lubricants can of course be employed including certain silica compounds and certain metal oxides. Suitable materials as lubricants are known to those working in this field.

The introduction of the inorganic lubricant material into

the zinc metal structure appears to be analogous to alloy formation, that is the inorganic lubricant molecules or groups of molecules are entrained into the zinc metal lattice structure so as to be inseparable by normal mechanical means.

In a preferred form of the process of the invention which produces composition of the invention a zinc powder or zinc dust is combined with carbon and milled, particularly by ball milling.

The initial zinc powder or zinc dust can have the particle sizes for zinc dust of less than 20 microns and for zinc powder 10 to 60 microns, zinc dust being preferred. The lubricant carbon particularly employed can be various forms of carbon but preferred is graphite of particle size of from 3 to 30 microns or conductive carbon black having particle size of from 1 to 3 microns (or even less). Other lubricants (particularly organic lubricants such as polyfluoroethylene) will have similar particle sizes.

The proportion of lubricant added will depend on the desired properties of the final composition. Particularly when the carbon is added by milling of zinc to form a flake there should be enough carbon added to act as a lubricant in the milling process in addition to its function in the final composition. For most lubricants including organic lubricants the amount added will be determined solely by the amount which achieves flaking in a reasonable time. A proportion of 1 to 10% by weight lubricant to metal appears to be very effective. For zinc to carbon 2 to 5% by weight is preferred and the optimum range is 3 to 5% by weight. The same ranges apply to organic lubricants. Conventional milling processes can be employed including ball mills, pebble mills and other mills used for making flake material, particularly zinc flake. The mill will be one in which the impact of the milling means especially grinding media reduces the thickness of the zinc particle to give flake form and not merely a mill which reduces particle size. Such mills are well known to those skilled in the art.

The term substantially dry conditions indicates that a small amount of liquid may be present at least initially to assist in blending the mixture, ie. distributing the lubricant over the metal but is very substantially different from the use of large volumes of solvent in previous milling of flake in which the solid materials are dispersed in the solvent/liquid phase. Under the substantially dry conditions of the process of the invention it is likely that any solvent will disappear during milling.

The process of the invention can be applied to other metals, for example brass possibly for use in water treatment techniques, copper, silver and aluminum. The metal should be one which is sufficiently malleable for the particles to substantially flatten upon milling. The process produces a low apparent density product.

In the case of zinc products, the resulting composition can be employed in coating compositions, particularly primers, for application to surfaces which are subject to corrosion. Such compositions contain binder resins, zinc anti-corrosive agent and other conventional or standard components of such compositions.

The flake products obtained by the process of the invention have provided zinc rich epoxy primers with a zinc flake to binder ratio of approximately 3 to 1 which have provided protection for in excess of 30 days, revealing no rust in the 6-8mm drilled holes over treated, passivated and blasted steel. All conventional zinc rich organic primer controls with a 9 to 1 zinc to binder ratio failed this test.

The following list describes several important or unique properties provided by this development to advance zinc rich coatings technology:

1. <u>Density</u> - The density at equal volume solids is reduced by as much as one half due to an effective lower zinc to binder ratio, while the PVC (Pigment Volume Concentration) is reduced

from over 50% to approximately 30%.

2. Cost - Up to a 50% lower raw material cost reduction at equal volume solids.

3. Sedimentation - Soft settling of the zinc is consistent throughout this development.

4. Application over Phosphated Steel - A dramatic increase in cathodic continuity and conductivity is effective in producing protective white rust to adjacent bare metal.

5. Flexibility - Organic zinc rich formulae including the powder development (powder coatings consistently provide 72kg (160lbs) front and reverse impact resistance, often a requirement for reinforcement bars or over coil coated steel that is to be postformed).

6. Deposition - The thixotropic properties of these primers permit depositions up to 75 microns without sagging.

7. Application Qualities - With the exception of the powder development all primers can be formulated for spray, brush, dip or rollercoat application.

8. Low Temperature Application - Vinyl chloride - isocyanate hybrid formulae have been developed for low temperature environments.

9. Ease of Recoatability - All development both inorganic and organic are recoatable with most solvent and waterborne topcoats.

10. User Friendly Inorganic Zinc primers - The manufacturing, packaging and storage of the single component inorganic moisture cured primer development (silicic acid esters) does not require a nitrogen blanket. These primers can be manufactured, packaged and applied without a nitrogen blanket preventing short term

gelation with repeated opening and closing of the container - compare US Patent 5,413,628 May 9th, 1995.

11. Colour Development - Primers containing zinc flake can be tinted to match most medium tone industrial primers.

12. Ease of Spot Welding - The ultra high conductivity of this development provides excellent welding properties.

13. VOC's (Volatile Organic Components) - Both the inorganic and organic primers have been formulated to achieve a VOC of 2.94 or lower.

14. Powder Application - This development is available in epoxy and polyester powders providing exceptional anti-corrosion resistance.

The use of zinc flaked by the process of the invention in manufacture of a corrosion-resistant composition has been found to provide a superior product to conventional zinc primers. Conventional zinc rich primers demonstrate little to no passage of current when tested over a dielectric (non-conductive) surface. Coatings with flaked zinc provide consistent cathodic conductivity throughout the primer surface and in particular a resistance reading of less than 20 K-ohms when tested over a dielectric. When electric resistance over a dielectric, for example a primed iron or zinc phosphated panel, registering 20 K-ohms is achieved, red rust is prevented for in excess of 500 hours using the ASTM, B-117 salt-fog test modified with several 8mm holes through the primer.

Conventional zinc rich epoxy coatings with 90% by weight zinc to binder develop total red rust on drilled areas within several hours under modified B117 salt-fog conditions.

A particular advantage of the modified zinc composition of the invention is that in milling the components (e.g. resin etc.) for a coating composition, the possibility of fusion of zinc

particles is avoided. This avoidance of fusion or sintering can eliminate or at least substantially reduce the need for anti-sintering agents particularly for powder coating compositions.

Binder resins used in compositions into which the zinc flake products produced by the invention are introduced will include alkyl silicates, zinc silicates, epoxy resins (powder and non-powder) and well known equivalents of these resins, including epoxy esters or polyester resins. Polyester powder resins may not be appropriate for solvent based compositions since they do not generally dissolve in common solvents.

For an epoxy powder coating composition the presence of a curing agent/hardener may be necessary, for example a bisphenol epoxy resin/diethylene triamine adduct together with propylene glycol monourethyl ether, N-butyl alcohol, toluene and di-ethylene triamine. Various commercial curing agents/hardeners are available. It may also be desirable to include a flow control agent, for example a polyacrylate and an electro-static charge modifier, for example aluminum oxide. The resin binder can be any of the well known resins which are soluble or easily dispersible in the solvent, for example an epoxy powder. Epoxy resins are the reaction products of epihalohydrin and phenols and hardening or crosslinking agents may be provided which contain functional groups reacting with the epoxy function. The preparation of epoxy resins and crosslinking reactions are described in US Patent 3,954,693 issued May 1976 to C.C. Fong to which reference is made and the disclosure of which is incorporated by reference. Preferably an epoxy powder as used in compositions containing zinc compositions of the invention have epoxide values (equivalent weight) of from 425 to 1000, more preferably 450 to 800. Another binder can be an alkyl silicate, for example ethyl silicate dissolved in ethanol (ethyl polysilicate/ethylene glycol monoethylether/ethanol). In such a composition a catalyst may be required to accelerate reaction between the silicate, the zinc and substrate and also a wetting agent can be employed.

A particularly useful binder which may have unusual aspects in the present invention is a zinc silicate. This could provide a water-borne composition and in particular a water-borne reactive primer which could even replace electrodeposition of zinc. The composition would comprise zinc silicate as binder and the flaked zinc produced by this invention.

Coatings of the present invention are particularly suited for use as cathodic coatings, zinc containing substance constituting the conductive phase when used as a "sacrificial anode". Coating compositions containing zinc compositions can be used for protection against corrosion on substrates including those in:

1. storage rolling stock;
2. dams, bridges and lift gates;
3. storage tanks; cylinders;
4. ships and port facilities;
5. guardrails;
6. transmission towers;
7. trucks' automotive parts and chassis;
8. silos and grain storage units;
9. light poles;
10. gutters and down spouts;
11. air conditioning equipment;
12. washers and driers;
13. wire fencing;
14. ducting;
15. corrugated metal and buildings having units constructed from such metal;
16. pipe, plumbing and tubing;
17. fasteners;
18. steel reinforcement bars, and
19. offshore drilling platforms.

However, these are merely listed as suggestions for applications of the final coatings prepared using the zinc material produced by the process of the present invention.

It should be appreciated that these comments on the specific nature of coating compositions are merely to illustrate the type of compositions in which the flaked zinc materials of the invention may be incorporated and are not intended to be restrictive of the application of the zinc compositions of the invention and their application. Thus the compositions could be used in anti-corrosion compositions for application to brass, aluminum, and other metals subject to corrosion.

A surprising effect of the invention is that coating compositions containing the modified zinc composition of the invention provide improved cathodic protection to so-called treated or passivated steel. Such steel, ie. steel treated with, for example, zinc or iron phosphates, represent virtually the majority of painted steel utilised in industrial applications. The zinc rich primer compositions presently employed do not provide protection to such passivated steel, ie. so-called white rust protection and are generally applied over blasted steel for industrial application. Steel which is to be painted for anti-corrosion protection is customarily sand blasted, for example when used in bridges, dams, ships, storage tanks etc. The inclusion of the carbon into intimate combination within the zinc particle is a particularly important feature of this aspect of the invention since simply combining zinc powder and free carbon, eg. graphite, while giving useful results requires high proportions of carbon, for example at least 30%, and/or high proportions i.e. from 30 to 60% by weight on binder that is 3 to 6% weight on a final coating composition as compared to 2% or less by weight with the present invention of zinc flake modified with carbon.

The introduction of the lubricants carbon (graphite) and polyfluoroethylene, apart from producing a superior final composition, has a dramatic effect on the time necessary for the milling of the zinc to a flake form. The ability to operate a mill, for example a pebble or ball mill, for only 12 to 36 hours on even a laboratory mill and about 5 hours in a commercial mill

is considerably lower than that with present milling techniques and therefore significantly reduces the cost of flake. Thus the use of the zinc composition of this invention provides an impressive reduction in cost and performance in the reduction of corrosion.

Coating compositions of the invention can contain proportions of the zinc material in amounts conventional for such compositions, for example over 5 parts by weight zinc to 1 part binder but in one preferred aspect of the invention the amount of zinc can be less than 65% by weight of the dry components (excluding solvent/liquid). An important attribute of the zinc flake particulate product is its low apparent density and the effect of this density on the composition.

The following Examples provide preferred embodiments of the various aspects of this invention simply by way of illustration, of some of the best modes contemplated for carrying out the invention. As will be realised, the invention is capable of modification in various, obvious aspects, all without departing from the invention. Accordingly, these Examples should be regarded as illustrative in nature and not restrictive.

Example 1

300g of 515 zinc dust (100% passes a 325 US standard mesh sieve), a commercial zinc dust known as Purity Zinc, and 9g of a commercial graphite A-99 comprising 98% carbon, particle size of 3% maximum of 44 mesh screen and density 2.25g/cc, provided by Asbury Graphite were loaded into a one third litre jar pebble mill together with 2.27 kg (5lbs) of 4.76 mm (3/16 inch) steel balls and milled, samples being taken during the course of milling.

The density of the dust as a result of the milling was as follows:-

Table 1

Time of Milling	Apparent Density gm/ml^3
Unmilled	3
12 hours	2
24 hours	1.6
32 hours	1.2

Thus the apparent density was reduced from 3g/ml^3 to 1.2g/ml^3.

The milled pigment changed during milling from a fine grey dust to a metallic flake with a golden hue.

A production commercial mill would be expected to achieve the same reduction about 3 times more quickly.

The resulting milled material was combined with a typical phenolic epoxy primer used in conventional primer compositions in the proportion of 3 parts of the modified zinc dust to 1 part binder by weight. A control was prepared using 9 parts unmodified zinc dust to 1 part epoxy phenolic binder. The two primers were separately applied over cold rolled steel panels and iron phosphated panels under the test conditions of ASTM B-117 (salt fog). The panels were then exposed for 500 hours.

The test panels coated with the modified zinc composition of the invention, ie. the milled zinc/graphic composition exhibited zero corrosion over the cold rolled steel and iron phosphated steel.

The conventional composition containing unmodified zinc also exhibited zero corrosion in the scribed areas of cold roll steel but rusted within hours over the iron phosphated panels.

A parallel series of tests were conducted employing an inorganic acid silica ester treated panel and the same results

were found.

This Example demonstrates that the presence of the graphite not only reduced zinc requirement by two thirds, but provided improved cathodic protection to passivated steel.

Example 2

The process of Example 1 was repeated but using instead of zinc dust a #1239 zinc powder produced by Zinc Corporation of America. The milling period was reduced from 32 hours to 24 hours and provided the same apparent density at the end of that time. The resulting product zinc-graphite powder had a more silvery appearance somewhat similar to conventional flake manufactured using inert hydrocarbon and stearic acid lubricant.

Example 3

The process of Example 1 was repeated employing two forms of commercial carbon black, one produced by Degussa and the other by Colombian Carbons. The resulting zinc/carbon compositions demonstrated the same results as outlined in Examples 1 and 2.

Example 4

Example 1 was repeated using 300g of Zinc Corporation of America Zinc powder #1239, average particle size 15 microns, 3% by weight A99 graphite and 1% or 3g of stearic acid using a grinding media of 20.6 mm (13/16 inch) pebbles of approximately 2.7 kg (6lbs), ie. 2.7 kg of pebble, 312g pigment. After 12 hours of milling the pigment had a bright leaf appearance similar to that produced by conventional milling techniques for much longer times but with a density of 2g/ml^3. Further milling for 6 hours provided a product which was consistently flake like but produced an apparent density less than 1.5g/ml comparable with the best conventional commercial products.

The modified zinc composition produced in Example 1 was incorporated into coating compositions as follows:-

Example 5

(Low VOC Coating Composition)

Percent by weight	Material	Supplier
20.0	Rezimac 57-5839 Epoxy Ester 70% solids weight	McWhorter
14.0	Mineral Spirits (low odor)	
35.0	Zinc Dust (Carbon modified)	Inventor
14.0	Zinc Dust #4	Purity
3.5	Chrome oxide GO-6099	Harcross Pigment
2.7	Sphericel Hollow Spheres 110-P8 (glass spheres)	PQ Corporation
0.4	BYK 410 (Flow Control Agent)	BYK Chemie
0.4	12% Cobalt Drier) Drying	Huls
1.1	12% Zirco Drier) Agents	Huls
0.7	Active 8 (Drying agent)	Vanderbilt Co.
0.2	Ekin - #2 (Anti-skin agent)	Huls
8.0	Acetone	Huls

100		

Example 6

Linear Epoxy Coating Composition

Percent by weight	Material	Supplier
32	DER 684-EK40 (Linear Epoxy)	Dow Chemical
32	Zinc flake (Carbon modified)	Inventor
12.8	Zinc Dust #4	Purity Zinc
0.38	BYK 410 (Flow Control Agent)	BYK Chemie
3.32	Chrome Oxide GO-6099	Harcross Pigment
19.5	P.M. Acetate (Water soluble acetate)	Eastman

100		

Example 7

Coating composition for application with baking of product

Percentage	Material	Supplier
11.8	DEH 642U (Phenolic Hardener)	Dow Chemical
5.8	DER 87 } (Phenolic	Dow Chemical
0.5	DER 82 } Hardener)	Dow Chemical
45.5	Zinc flake (Carbon Modified)	Inventor
18.2	Zinc Dust #4	Purity Zinc
4.5	Chrome Oxide GO-6099	Harcross Pigment
0.7	BYK 410 (Flow Control Agent)	BYK Chemie
7.5	MIBK (Methyl iso-butyl ketone)	
5.5	XYLOL	

100		

Example 8

Two component composition for air-drying

Percentage	Material	Supplier
10.8	1001 F	Shell Chemical
5.4	DEH 87 (Phenolic Hardener)	Dow Chemical
45.0	Zinc flake (Carbon Modified)	Inventor
18.0	Zinc Dust #4	Purity Zinc
3.6	Chrome Oxide	Harcros Pigment
0.7	BYK 410 (Fow Control Agent)	BYK Chemie
7.2	MIBK	
5.4	XYLOL	
	Part B	
1.8	Cardolite NC-560 (Polyamide curing agent)	Cardolite Corp.
2.1	MIBK	

100		

Example 9

Inorganic ethyl silicate bonded composition

Percentage	Material	Supplier
38.8	Silbond H-12A (Ethyl Silicate Solution)	Silbond
33.5	Zinc flake (Carbon Modified)	Inventor
20.0	Zinc Dust #4	Purity Zinc
2.5	Chrome Oxide GO-6099	Harcros Pigment
0.7	BYK 410 (Flow Control Agent)	BYK Chemie
4.5	TEOS (Tetraethoxysilane) (Stabiliser)	

100		

Each of the compositions in the above Examples produced final coatings with excellent anti-corrosion properties despite the reduction in content of zinc.

Example 10

Production of flaked brass

500 gms of powdered commercial brass was mixed with 2% by weight of brass of graphite and milled in a laboratory sized steel ball mill as in Example 1 for 24 hours. The apparent density was reduced 66%. The product when introduced into a water treatment column gave a satisfactory result despite the reduced total weight of brass in the column.

Example 11

Silver powder is subjected to a treatment as in Example 10. A final flaked product is obtained which is of reduced apparent density.

Example 12

Example 1 is repeated with, as inorganic lubricants:

(1) Fumed Silica "Aerosil" supplied by Degussa;

(2) A commercial aluminum oxide of fine particle size.

Satisfactory products are obtained in which the product is of

flake form and the majority of the lubricant is incorporated into the metallic zinc structure.

Example 13

10 grams of a zinc silicate binder (WB-18 No-cure water based zinc silicate supplied by International Zinc, Coatings & Chemical Corp.) was mixed with

(1) 30g of a zinc dust/mica mixture containing conventional powdered zinc dust;

(2) 15g of a modified zinc according to the invention sized through a 325 mesh (US Standard Sieve) screen.

Both compositions were applied to untreated cold rolled steel and tested in accordance with Example 1.

The conventional composition (zinc dust/mica) showed considerable corrosion within 48 hours.

The composition with the zinc flake of the invention resisted corrosion for a much longer time; unaffected after 200 hours.

Example 14

Basic procedure for the manufacture of a 500 gram sample or a production batch of product according to the invention.

To 500 grams of zinc dust of Purity Zinc's dust #4 (average particle size 4 microns) were added 20 grams or 4% of Asbury Graphite's A-99 (average particle size ± 20 microns). The function of the graphite is twofold: 1. As the principal dry lubricant, 2. To impart increased conductivity to the final flake to improve cathodic properties (bare metal protection) 5 grams or 1% of Degussa's Hydrophobic Aerosil 972 was added to the mix. Its function is again twofold: 1. To improve slip resistance during the milling process, thereby reducing heat exotherm during processing (a potential fire hazard), 2. To provide thixotropic properties to the final zinc flake to improve anti-settling properties when added to an appropriate binder. To the above mix was added 2½ grams of aluminum oxide which also

serves two functions:

1. To reduce potential sintering or sticking to the grinding media or to the sides of the ball mill
2. To improve electrostatic properties when the zinc flake is utilised in a powder application.

This mixture was well blended prior to addition to the ball mill containing approximately 4.5 kg (10 lbs) of steel ball as a grinding media. The ball mill was then operated between 6 to 12 hours depending upon the desired apparent density of the zinc flake required. The longer the mill was in operation the lighter the apparent density of the average zinc flake particle. The lighter the apparent density, the larger the volume of zinc flake which is produced, and this inversely reduces the corresponding weight of flake to binder required to perform appropriate cathodic protection. However, certain binders require a higher or lower ratio of flake to produce special properties, consequently various average particle size zinc flake will be made available to industry.

After the desired apparent density had been achieved, the mixture that had been transformed into zinc flake was <u>completely vacuumed from the ball mill</u> leaving only the grinding media within the mill. All objectionable particle sizes were separated by a Vorti-Sieve over which a specific mesh screen had been placed to prevent oversized particles from inclusion in the final product. The produced zinc flake was then packaged for sale or distribution.

<u>Example 15</u>

Zinc dust (a commercial zinc dust Purity® 15G supplied by North American Zinc Company (Purity Zinc Metals Division) and average particle size 10 microns) was mixed thoroughly with 2 percent by weight of zinc of polytetrafluoroethylene of specific gravity 2.15 melt point 320°C supplied under the trade name Fluoro A by Shamrock Technologies Inc., Pacific St., Newark, New Jersey

07114, USA.

Samples of the mixture were ball milled for 6 to 10 hours depending on particle size (flake) and desired final density. The flake had an aluminum (bright) appearance; coating compositions containing the flake demonstrated excellent corrosion resistance though less than that of zinc flaked with graphite. The longer the milling the better the brightness and lower the apparent density of the final flake. Similar results were obtained using zinc powder (Product 1239 supplied by Zinc Corporation with particle size 20 microns).

Example 16

Example 15 was repeated using as lubricant a blend of the polytetrafluoroethylene M290 (1% by weight of zinc), graphite (A99 supplied by Asbury Graphite particle size 20 microns - 1% by weight of zinc) and mica (1% by weight of zinc; particle size 6 microns - supplied as Alsibronz o6 supplied by Engelhard Corporation). The resulting flaked product was about as effective as a product milled only with polytetrafluoroethylene (3% by weight zinc) but was less expensive to produce.

CLAIMS

1. A method for the preparation of a metal material comprising a metal which is sufficiently malleable for its particles to flatten when subjected to mechanical milling, characterised in that it comprises a step in which a mixture of particles of the metal and a solid composition with lubricant properties is subjected to mechanical milling under substantially dry conditions until the metal is in the form of flakes.

2. A method according to claim 1 characterised in that the metal is zinc.

3. A method according to claim 1 or claim 2 characterised in that the metal is zinc and the solid lubricant composition is an inorganic solid lubricant affecting the cathodic properties of zinc.

4. A method according to claim 3 characterised in that the inorganic lubricant composition is a graphite or carbon black.

5. A method according to claim 4 wherein the milling is continued until the metal is in flake form and a major proportion of the graphite or carbon black is incorporated into the metal lattice structure.

6. A method according to either of claims 1 and 2 wherein the solid lubricant is a high molecular weight organic solid lubricant substantially free of interfering functionality.

7. A method according to claims 6 in which the solid lubricant is a solid organic polymer with solid lubricant properties.

8. A method according to any one of claims 1 to 7 characterised in that the mixture of malleable metal and solid lubricant contains from 1 to 5% by weight of solid lubricant by weight of metal.

9. A method according to any one of the preceding claims characterised in that the metal flake product is combined with conventional binder components to form a composition for application to form a corrosion resisting coating.

10. A finely divided metal flake material characterised in that it comprises particles in flake form of a metal which is sufficiently malleable for particles thereof to flatten when subjected to mechanical milling and a solid inorganic lubricant, a major proportion of the lubricant being incorporated into the lattice structure of the metal.

11. A material according to claim 10 characterised in that the metal is zinc.

12. A material according to claim 10 or claim 11 characterised in that the content of the lubricant is from 3 to 5% by weight of the metal.

13. An anti-corrosion coating composition characterised in that it contains finely divided zinc particulate flakes and carbon, a major proportion of the carbon being incorporated into the zinc lattice structure.

14. An anti-corrosion coating composition according to claim 13 characterised in that it contains zinc flakes of thickness 1 micron or less, an aspect ratio of 10 and 1 to 10% by weight carbon.

15. A method of preparing an anti-corrosion coating composition comprising the steps of:

(1) mixing zinc particles with particles of solid components with solid lubricant properties;
(2) subjecting the mixture to mechanical milling under substantially dry conditions to render the particles into lamellar shape; and
(3) combining said lamellar shaped particles with binder

components to form a coating composition applicable to a substrate to form a corrosion resistant surface layer.

16. A method according to claim 15 wherein the binder components include a silicate water-borne binder.

INTERNATIONAL SEARCH REPORT

In tional Application No
PCT/US 99/06647

A. CLASSIFICATION OF SUBJECT MATTER
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B22F C09C C09D C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 389 105 A (BOLGER WILLIAM T) 18 June 1968 (1968-06-18) column 1, line 11 - column 2, line 2 example 1 claims ---	1,6-8
X	US 2 432 465 A (BABCOCK G M) 9 December 1947 (1947-12-09) column 1, line 1 - column 2, line 2 column 2, line 16 - line 22 column 3, line 2 - line 20 ---	1,2,8, 10-12, 15,16
	-/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
30 July 1999	19/08/1999

Name and mailing address of the ISA	Authorized officer
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

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